Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Mesomorphic amino sugars

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To cite this Article Stangier, P. , Vill, V. , Rohde, S. , Jeschke, U. and Thiem, J.(1994) 'Mesomorphic amino sugars', Liquid Crystals, 17: 4, 589 — 595
To link to this Article: DOI: 10.1080/02678299408036743
URL: http://dx.doi.org/10.1080/02678299408036743

LIQUID CRYSTALS, 1994, VOL. 17, NO. 4, 589–595

Mesomorphic amino sugars

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(*Received 3 September 1993; in final form 1 May 1994; accepted 10 May 1994*)

New liquid crystalline compounds have been prepared from glucosamine and 6-amino-6-deoxy-hexopyranoses. The monoalkylated carbohydrates show smectic phases. The influence of the amino group on the clearing temperatures is minor. The salts of the cyclic amines can form smectic or discotic mesophases. The clearing points are lower than those observed for acyclic amines.

For some two years, liquid crystalline carbohydrate derivatives have been intensively investigated [1]. Along with the mesomorphic properties, the surfactant properties and biological functions are of particular relevance. However, knowledge about structure–property relationships is still poor to date.

Amphiphilic amino sugars such as phytosphingolipids [2] are interesting naturally occurring compounds, but their thermotropic liquid crystalline properties have not yet been studied. There are a few examples of synthetic liquid crystalline amino sugars known at present: *N*-alkylglucosylamines [3], *N*-alkyl-1-aminoglycerides [4] and *N*-alkylglucamines [3, 5]. In all of these compounds, the secondary amino group is the bridge between the hydrophilic and the hydrophobic part, A direct comparison with ether analogues is possible for the alkylglucamines and the 1-sorbitol ethers [6] only. Here, the amino compounds show clearing points approximately 10–15°C higher than the oxygen compounds. A particular property of the amino sugars is their ability to form mesomorphic salts [5].

Therefore, liquid crystalline carbohydrates with a primary amino group located in the hydrophilic part of the molecule have now been studied. It was considered that alkylglucosamines especially should be suited to observe such effects, and together with simple compounds, bola-amphiphiles and alkyl-modified compounds have been prepared and intra- and inter-molecular salts studied. For comparison, 6-amino-6-deoxy-sugars are also listed.

All 2-amino-2-deoxy-glucopyranosides have in common a high melting point and their melts show a low tendency to be supercooled. Their solubility is very high in almost all solvents. The properties of the simple *N*-alkylglucosamines are presented in table 1 and compared with the alkyl glucosides. Both homologous series generally show S_A phases with lower clearing points for the amino compounds. Temperatures in

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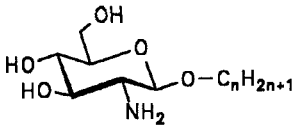
0267–8292/94 $10·00

Table 1. *n*-Alkylglucosamines (**1**).



No.	*n*	Phase transitions/°C						Analogous alkyl β-glucopyranoside [7]				
1.8	8	(93)	C	118·3	X	94·3	I	C	67·1	S_A	106·4	I
1.9	9	(98)	C	118			I	C	68	S_A	113	I
1.10	10	(95)	C	118·7	X	96·6	I	C	70·3	S_A	133·5	I
1.12	12	(98)	C	102·2	S_A	125·2	I	C	80·4	S_A	143·4	I
1.14	14	(80)	C	90·2	S_A	125	I					
1.18	18	(100)	C	118·6			I					

C = crystalline, I = isotropic liquid, S_A = smectic A, X = unidentified liquid crystalline phase.

parentheses in column three relate to recrystallization on cooling (also in tables 2 and 4).

The introduction of a small polar head group into the alkyl chain leads to '1·5 fold amphiphilic' compounds. In table 2, the ω-hydroxy compounds are listed. Only the derivative with the long chain, **2.16**, shows a smectic phase with a low clearing point. If a terminal carboxy group is introduced, the amino acid, **3** (see table 3) is obtained. This exhibits internal salt formation and melts at the very high temperature of 237°C with decomposition. The introduction of a second sugar unit leads to the bola-amphiphilics, **4** (see table 4) and none of the compounds prepared exhibited liquid crystalline properties.

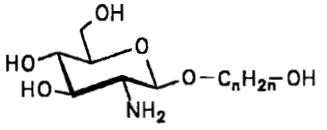
A particular feature of the liquid crystalline amino compounds is the ability for salt formation with organic acids. Smectic *N*-alkylglucamines and long chain acids gave discotic salts with high clearing points [5]. Obviously this reaction had to be confirmed for the glucosamines now under discussion.

A very simple salt is the hydrochloride, **5** (see table 5). As this compound has a high polarity and only one alkyl chain, a S_A phase with a high clearing point can be observed.

The salt formation with organic acids was studied using contact preparations. Some of the results with *n*-dodecylglucosamine, **1.12**, are summarized in table 6. With 4-dodecyloxybenzoic acid, an optically isotropic and supposedly cubic phase can be prepared. Columnar discotic phases can be obtained either with a monoalkylphosphoric acid or with a perfluoroalkanoic acid. In every case, the isotropic transition temperature of the generated phase is low and the range of concentration of their existence is narrow. Compounds of α,ω-diglucosaminyloxyalkanes, **4**, gave no mesomorphic salts in our experiments. We also tested glucosamine derivatives with short chain aglycons (see table 7 and table 8). Only with the shortest chain aglycons were liquid crystals obtained and the clearing point was highest with the perfluorinated acid.

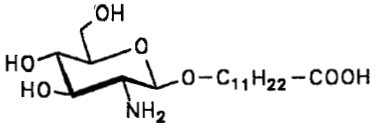
Alkyl 6-acylated glycopyranosides are known to form discotic liquid crystals with β-glycosides and have higher clearing points than those with α-glycosides [8]. Here, it was intended to use an amino group to connect a second alkyl chain to simple glucosides. The neutral amines, **6a** and **6b** (table 9) form isotropic syrups at room temperature. Likewise, octyl 6-decanoyl-α-D-glucopyranoside [8] has a clearing

Table 2. ω-Hydroxyalkylglucosamines (**2**).



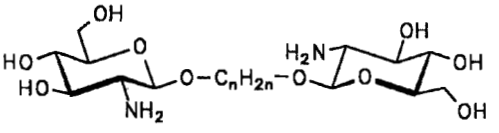
No.	*n*	Phase transitions/°C				
2.9	9	(90)	C	115·9		I
2.16	16	(100)	C	122·3	(S_A 103·5)	I

Table 3. 11-(2-Deoxy-2-amino-β-D-glucopyranosyl)dodecanoic acid (**3**).



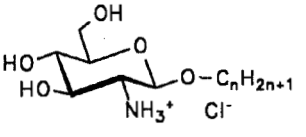
No.	*n*	Phase transition/°C		
3	11	C	237	decomposed

Table 4. α,ω-Diglucosaminyloxyalkanes (**4**).



No.	*n*	Phase transitions/°C			
4.9	9	(94)	C	118·5	I
4.10	10	(90)	C	118·3	I
4.12	12	(96)	C	118·0	I
4.16	16	(98)	C	115·3	I

Table 5. Hydrochloride (**5**).



No.	*n*	Phase transition/°C				
5	12	C	129	S_A	199	I

Table 6. Contact preparations of **1.12**.

Acid	Phase behaviour
$C_{12}H_{25}$–O–C_6H_4–COOH	Smectic A up to 126·5°C and isotropic phase (cubic ??)
$C_{10}H_{21}$–OPO_3H_2	Discotic up to 103°C in a small range of concentration
C_9F_{19}–COOH	Discotic up to 138°C

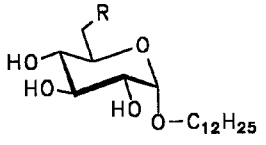
Table 7. Contact preparations of methyl 2-amino-2-deoxy-α-D-glucopyranoside.

Acid	Phase behaviour
$C_{12}H_{25}$–O–C_6H_4–COOH	Smectic A up to 153°C
C_9F_{19}–COOH	Discotic and smectic A above 200°C

Table 8. Contact preparations of pent-4-enyl 2-amino-2-deoxy-β-D-glucopyranoside.

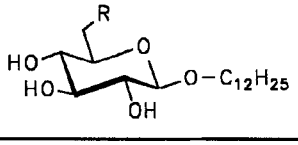
Acid	Phase behaviour
C_8H_{17}–C_6H_4–COOH	No mesophase
$C_{18}H_{37}$–O–C_6H_4–COOH	No mesophase

Table 9. 6-Alkylamino-6-deoxy-α-D-glucopyranosides (**6**).



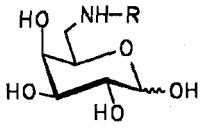
No.	*R*	Phase transitions/°C				
6a	NH–C_3H_7	C	< 20			I
6b	NH–C_8H_{17}	C	< 20			I
6c	$^+NH_2$–$C_3H_7Cl^-$	C	?	S_A	113·5	I
6d	$^+NH_2$–$C_8H_{17}Cl^-$	C	< 90	S_A	148·6	I

Table 10. 6-Alkylamino-6-deoxy-β-D-glucopyranosides (**7**).

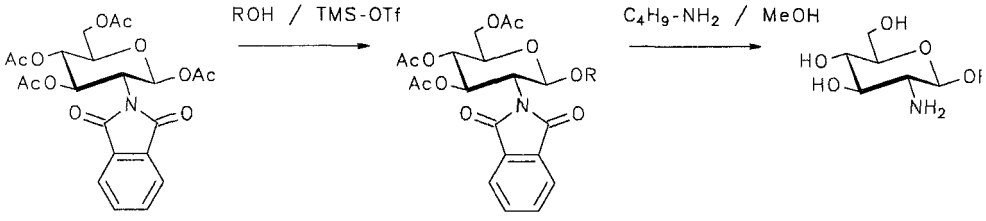


No.	*R*	Phase transitions/°C				
7a	$^+NH_2$–$C_3H_7Cl^-$	C	?	S_A	174	dec. [11]
7b	$^+NH_2$–$C_8H_{17}Cl^-$	C	?	S_A	> 174	dec.

Table 11. 6-Amino-6-deoxy-D-galactoses (**8**).



No.	*R*	Phase transitions/°C
8a	SO_2–$C_{16}H_{33}$	C 142 S_A 235 I
8b	CO–$C_{17}H_{35}$	C 133·6 S_A 197·1 I



Scheme.

temperature below room temperature. The hydrochlorides **6c**, **6d**, **7a** and **7b** form smectic liquid crystals, and again, the β-glycosides have higher clearing temperatures than the α-anomers (see tables 9 and 10).

The amides of 6-amino-6-deoxygalactose have only one alkyl chain connected at the amino group and consistently, they form smectic A phases. The clearing temperatures are higher (see table 11) than those of the alkyl glucosides (see table 1). The sulphonamide, **8a**, has a higher clearing temperature than the carbonamide, **8b**, because of an enhanced contrast in polarity [5].

These findings result in the following résumé. In order to induce high clearing points, an amino group should be located at the bridge position between the hydrophilic and the hydrophobic area. However, positioned in the hydrophobic part, the amino group can lead to a slight decrease in the clearing point. A particular property of the amino sugars is their ability to form salts. Depending on the acid used, smectic, discotic or cubic phases can be prepared. The clearing points of the flexible open chain compounds are higher than those of the stiff cyclic compounds.

The transition temperatures were determined using a polarizing microscope (Olympus BH) equipped with a heating stage (Mettler FP 82). The phase assignments were based on characteristic textures and miscibility studies with reference compounds. In all cases, the smectic A phases show homeotropic and simple fan-like textures. Uncovered samples form stepped drops. The smectic A phases of all amino sugars are miscible with the smectic A phase of dodecyl β-D-glucopyranoside [7].

The syntheses were performed according to the scheme. TMS triflate was used as catalyst for the glycosylation of tetra-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranose [9]. Butylamine was used for the deprotection of the glycosides [10]. All compounds were purified by repeated crystallizations from ethanol and were thoroughly characterized by NMR.

Physical data for some of the new compounds are now given as examples.

Octyl 3,4,6-tri-O-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranoside

Yield: 91 mg (20 per cent), isotropic oil. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 5{\cdot}37$ (d, 1 H, H-1), 4·32 (dd, 1 H, H-2), 5·81 (dd, 1 H, H-3), 5·18 (t, 1 H, H-4), 3·88 (ddd, 1 H, H-5), 4·35 (dd, 1 H, H-6 a), 4·18 (dd, 1 H, H-6 b), 7·73–7·89 (2m, 4 H, $-C_6H_4-$), 1·87, 2·04, 2·11 (3s, 9 H, OAc), 3·84 (dt, 1 H, H_{Alkyl}-1 a), 3·44 (dt, 1 H, H_{Alkyl}-1 b), 0·80–1·52 (m, H_{Alkyl}-2–7), 0·81 (t, H_{Alkyl}-8); $J_{1,2} = 8{\cdot}5$, $J_{2,3} = 11{\cdot}0$, $J_{3,4} = 9{\cdot}5$, $J_{4,5} = 10{\cdot}0$, $J_{5,6a} = 5{\cdot}0$, $J_{5,6b} = 2{\cdot}0$, $J_{6a,6b} = 12{\cdot}0$, $J_{Alkyl\ 1a,1b} = 9{\cdot}5$, $J_{Alkyl\ 1a,2} = 6{\cdot}0$, $J_{Alkyl\ 1b,2} = 7{\cdot}0$, $J_{Alkyl\ 9,10} = 7{\cdot}5$ Hz.

^{13}C NMR (100 MHz, $CDCl_3$): $d = 98{\cdot}24$ (C-1), 54·73 (C-2), 70·87 (C-3), 69·15 (C-4), 71·87 (C-5), 62·12 (C-6), 167·52 (N–(C=O)$_2$–C_6H_4), 131·48 (N–(C=O)$_2$–C_2(CH)$_4$), 134·29, 123·56, (N–(C=O)$_2$–C_2(CH)$_4$), 170·66, 170·13, 169·49 (O–(C=O)–CH_3), 20·74, 20·62, 20·45 (O–(C=O)–CH_3), 70·15 (C_{Alkyl}-1), 31·63, 29·69, 29·65, 29·35, 25·75, 22·61 (C_{Alkyl}-2–7), 14·11 (C_{Alkyl}-8).

Octyl 2-deoxy-2-amino-β-D-glucopyranoside (**1.8**)

^{1}H NMR (400 MHz, MeOD): $\delta = 4{\cdot}23$ (d, 1 H, H-1), 2·43 (dd ~ t, 1 H, H-2), 3·10–3·21 (m, H-3, H-4, H-5), 3·67–3·79 (m, 2 H, H-6a, H-$_{Alkyl}$-1 a), 3·50 (dd, 1 H, H-6b), 3·34 (dt, 1 H, H_{Alkyl}-1 b), 0·80 (t, H_{Alkyl}-8); $J_{1,2} = 8{\cdot}0$, $J_{5,6b} = 5{\cdot}0$, $J_{6a,6b} = 12{\cdot}0$. $J_{Alkyl\ 1a,Alkyl\ 1b} = 9{\cdot}5$, $J_{Alkyl\ 1b,\ Alkyl\ 2} = 7{\cdot}0$ Hz.

1-(3,4,6-Tri-O-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyloxy)nonan-9-ol

^{1}H NMR (400 Mhz, $CDCl_3$): $\delta = 5{\cdot}35$ (d, 1 H, H-1), 4·28–4·36 (m, 2 H, H-2, H-6 a), 5·79 (dd, 1 H, H-3), 5·17 (t, 1 H, H-4), 3·86 (ddd, 1 H, H-5), 4·18 (dd, 1 H, H-6 b), 7·69–7·88 (2m, 4 H, $-C_6H_4-$), 1·86, 2·03, 2·11 (3s, 9 H, OAc), 3·83 (dt, 1 H, H_{Alkyl}-1 a), 3·43 (dt, 1 H, H_{Alkyl}-1 b), 0·80–1·52 (m, H_{Alkyl}-2–8), 3·57 (t, 2 H. H_{Alkyl}-9); $J_{1,2} = 8{\cdot}5$, $J_{2,3} = 10{\cdot}0$, $J_{3,4} = 9{\cdot}0$, $J_{4,5} = 7{\cdot}5$, $J_{5,6a} = 4{\cdot}5$, $J_{5,6b} = 2{\cdot}0$, $J_{6a,6b} = 12{\cdot}5$, $J_{Alkyl\ 1a,1b} = 9{\cdot}5$, $J_{Alkyl\ 1a,2} = 7{\cdot}0$, $J_{Alkyl\ 1b,2} = 6{\cdot}8$, $J_{Alkyl\ 8,9} = 7{\cdot}0$ Hz.

^{13}C NMR (100 MHz, $CDCl_3$): $d = 98{\cdot}24$ (C-1), 54·72 (C-2)70·86 (C-3), 69·14 (C-4), 71·85 (C-5), 62·14 (C-6), 167·78 (N–(C=O)$_2$–C_6H_4), 131·47 (N–(C=O)$_2$–C_2(CH)$_4$), 134·29, 123·59 (N–(C=O)$_2$–C_2(CH)$_4$), 170·77, 170·21, 169·50, (O–(C=O)–CH_3), 20·78, 20·64, 20·48 (O–(C=O)–CH_3), 70·12 (C_{Alkyl} − 1), 32·73, 29·32, 29·19, 29·17, 29·01, 28·95, 25·73 (C_{Alkyl}-2–8), 62·99 (C_{Alkyl}-9).

1-(2-Deoxy-2-amino-β-D-glucopyranosyloxy)nonan-9-ol (**2.9**)

^{1}H NMR (400 MHz, MeOD): $\delta = 4{\cdot}28$ (d, 1 H, H-1), 2·60 (dd ~ t, 1 H, H-2), 3·31–3·12 (m, H-3, H-4, H-5), 3·71–3·87 (m, 2 H, H-6 a, H-$_{Alkyl}$-1 a), 3·59 (dd, 1 H, H-6 b), 3·40–3·53 (m, 3 H, H_{Alkyl}-1 b, H_{Alkyl}-9); $J_{1,2} = 8{\cdot}0$, $J_{5,6b} = 4{\cdot}5$, $J_{6a,6b} = 11{\cdot}5$ Hz.

1,9-Bis(3,4,6-tri-O-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)nonane

Yield: 50 per cent, isotropic oil. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 5{\cdot}35$ (d, 2 H, H-1′, H-1″), 4·32 (dd, 2 H, H-2′, H-2″), 5·79 (dd, 2 H, H-3′, H-3″, 5·18 (t, 2 H, H-4′, H-4″), 3·87 (ddd, 2 H, H-5′, H-5″), 4·32 (dd, 2 H, H-6 a′, H-6 a″), 4·16 (dd, 2 H, H-6 b′, H-6b″), 7·68–7·89 (2m, 8 H, $-C_6H_4-$), 1·87, 2·03, 2·11 (3s, 18 H, OAc), 3·81(dt, 2 H, H_{Alkyl}-1 a H_{Alkyl}-9 a), 3·40 (dt, 2 H, H_{Alkyl}-1 b, H_{Alkyl}-9 b), 0·78–1·45 (m, H_{Alkyl}-2–8); $J_{1',2'} = J_{1'',2''} = 8{\cdot}5$, $J_{2',3'} = J_{2'',3''} = 10{\cdot}5$, $J_{3',4'} = J_{3'',4''} = 9{\cdot}0$, $J_{4',5'} = J_{4'',5''} = 10{\cdot}0$,

$J_{5',6a'} = J''_{5'',6a''} = 4{\cdot}5$, $J_{5',6b'} = J_{5'',6b''} = 2{\cdot}5$, $J_{6a',6b'} = J_{6a''6b''} = 12{\cdot}5$, $J_{\text{Alkyl 1a,1b}} = J_{\text{Alkyl 9a,9b}} = 9{\cdot}5$, $J_{\text{Alkyl 1a,2}} = J_{\text{Alkyl 9a,8}} = 7{\cdot}0$, $J_{\text{Alkyl 1b,2}} = J_{\text{Alkyl 9b,8}} = 6{\cdot}5$ Hz.

^{13}C NMR (100 MHz, $CDCl_3$): $d = 98{\cdot}25$ (C-1), 54·71 (C-2), 70·83 (C-3), 69·12 (C-4), 71·86 (C-5), 62·12 (C-6), 167·70 (N–(C=O)$_2$–C_6H_4), 131·40 (N–(C=O)$_2$–C_2(CH)$_4$), 134·36, 123·56 (N–(C=O)$_2$–C_2(CH)$_4$), 170·70, 170·15, 169·48 (O–(C=O)–CH_3), 20·76, 20·63, 20·46 (O–(C=O)–CH_3), 70·13 (C_{Alkyl}-1,9), 29·68, 29·24, 29·18, 25·72 (C_{Alkyl}-2–8).

1,9-Bis(2-deoxy-2-amino-β-D-glucopyranosyl)nonane (**4.9**)

^{1}H NMR (400 MHz, MeOD): $\delta = 4{\cdot}19$ (d, 1 H, H-1) 2·52 (dd ~ t, 1 H, H-2), 3·11–3·29(m, H-3, H-4, H-5), 3·72–3·87 (m, 2 H, H-6 a, H-$_{\text{Alkyl}}$1 a), 3·58 (dd, 1 H, H-6 b), 3·43 (dt, 1 H, H_{Alkyl}-1 b); $J_{1,2} = 8{\cdot}0$, $J_{5,6b} = 5{\cdot}0$, $J_{6a,6b} = 12{\cdot}0$, $J_{\text{Alkyl 1a,Alkyl 1b}} = 9{\cdot}5$, $J_{\text{Alkyl 1b,Alkyl 2}} = 7{\cdot}0$ Hz.

Support of this study by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

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